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Bio-inspired Metallo-supramolecular Polymers for Combined Mechanical Properties

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ARL-TR-5069   **January 2010**

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REPORT DOCUMENTATION PAGE			*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
January 2010	DRI	FY09

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Bio-inspired Metallo-supramolecular Polymers for Combined Mechanical Properties	
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
Robert H. Lambeth, Kenneth E. Strawhecker, and Joshua A. Orlicki	
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Research Laboratory ATTN: RDRL-WMM-A Aberdeen Proving Ground, MD 21005	ARL-TR-5069

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The development of materials with combined mechanical properties remains a significant challenge in polymer synthesis. The preparation of such materials could potentially impact a wide range of Army applications. In this work, bio-inspired metallo-supramolecular polymers were designed, synthesized, and characterized. We anticipate these polymers will display enhanced mechanical properties due to the presence of intermediate strength metal-ligand bonds present in the polymer backbone, which forms a compacted, modular molecular topology. The 2,6-bisbenzimidazolylpyridine ligand was prepared and incorporated into a model polymer backbone via thiol-ene click chemistry. The resulting polymer was thoroughly characterized by [1]H Nuclear Magnetic Resonance (NMR), gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). Binding of the ligand with Zn^{2+} and Co^{2+} was studied using ultraviolet/visible (UV/Vis) spectroscopy, which demonstrated a 2:1 ligand-to-metal ratio.

15. SUBJECT TERMS
Bio-inspired, metal-ligand, thiol-ene click chemistry, supramolecular polymer

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Robert H. Lambeth
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU	20	19b. TELEPHONE NUMBER *(Include area code)* (410) 306-0281
Unclassified	Unclassified	Unclassified			

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1. Objective

Many applications require materials to display high mechanical strength without sacrificing fracture toughness or ductility. Rigid polymer backbones and networks typically display high modulus but a poor ability to dissipate energy, resulting in failure at relatively small extension. Flexible materials often possess good extensibility due to their ability to dissipate energy but often display low modulus and stress response. Thus, the preparation of stiff materials with inherent mechanisms for stress dissipation remains a challenging target. The goal of this project is to develop bio-inspired modular metallo-supramolecular domains for incorporation into linear and cross-linked polymer backbones. This project primarily focuses on the design, synthesis, and characterization of highly tunable tethered metal-ligand bonds and their effect on material strength, toughness, and elasticity when integrated into polymer backbones. The incorporation of these modular domains into polymer backbones and networks is anticipated to provide a new generation of materials with superior modulus, tensile strength, and extensibility.

2. Approach

Polymers are ubiquitous in Army applications and are integral components of adhesives, composite armor packages, and ballistic impact resistant materials. In each case, the ability of the material to absorb and dissipate energy through various mechanisms is a very important function. Increasing the amount of energy a polymer can absorb before yielding would lower the required amount of material needed to meet specified criteria. The advantages of lighter, stronger materials are significant, especially in combat situations where reductions in weight make for a more mobile and agile warfighter and enhancements in blast mitigation reduce the trauma associated with blast loading and projectile impacts.

Energy absorption in polymers occurs primarily through two orthogonal characteristics: ductility and stiffness. Increasing either the ductility or stiffness (or both) without sacrificing the orthogonal characteristic will enhance the energy absorbing ability of the material. However, this is rarely the case, as increasing the ductility of a polymer is usually accompanied by a decrease in the stiffness (or vice versa). Thus, a longstanding challenge in polymer chemistry is to develop materials where typical tradeoffs in mechanical properties such as strength, stiffness, ductility, and fracture toughness are overcome.

This Director's Research Initiative (DRI) looks to nature for inspiration on designing materials possessing tailored mechanical properties. Biopolymers, such as spider dragline silk or sarcomere muscle titan, are dramatic examples of how nature has designed materials with a combination of exceptional stiffness, strength, toughness, and ductility. In both cases, weak

supramolecular interactions programmed into the protein structure provide energy dissipating mechanisms when the material is stressed (*1*). In particular, titan posses a linear array of modular, hydrogen-bonded domains that sequentially unfold, dissipating the energy built up along the protein backbone during elongation and providing good mechanical strength and fracture toughness (*2, 3*). Upon the release of stress, the domains reversibly fold, causing the extended chains to retract, thus providing elastic behavior (*4*). Single molecule force studies using atomic force microscopy (AFM) have demonstrated this remarkable mechanism for energy dissipation in the form of saw-tooth patterns in force-extension curves (*5*).

Guan and co-workers (*5, 6*) have recently demonstrated the use of modular multi-domain structures in synthetic polymers as a viable strategy for preparing materials with enhanced mechanical properties. Their design is based on double-tethered, quadruple hydrogen-bonded motifs arranged in a linear array along a polymer backbone. Similar to muscle titan, the hydrogen-bonded domain can reversibly rupture under an applied stress, providing a mechanism for energy dissipation that doesn't lead to material damage or failure. Single molecule force studies, dynamic mechanical analysis (DMA), and stress-strain analysis revealed mechanical properties similar to those observed in muscle titan. Further, upon plastic deformation of the material, the polymer was observed to recover its original length over time, suggesting a self-healing capability (*7*). Despite the remarkable properties observed in these synthetic materials, the system is not without significant drawbacks. Hydrogen bonds are generally thermally labile and water sensitive, limiting their application in military applications. Further, the hydrogen-bonded domains require a significant number of synthetic steps, which may prevent cost-effective scale up. Moreover, tuning of the supramolecular interaction is limited due to the additional synthetic steps that would be required to increase the number of hydrogen bonds between units.

Our goal was to take advantage of the design concepts for programming weak, non-covalent interactions for combined enhancements in mechanical properties and energy-dissipation introduced by Guan and coworkers and avoid the drawbacks associated with hydrogen-bonded systems. Thus, we proposed to use functionalized metal-ligand bonds as a platform for incorporating programmed non-covalent bonds into polymer backbones. Metal-ligand coordinated bonds are highly directional and the strength of the metal-ligand bond can be readily tuned by varying the metal-ligand combination and structure of the ligand itself. Compared to hydrogen bonds, metal-ligand bonds have been demonstrated to be more robust under shear stress (*8*). Moreover, the presence of counter-ions can affect the assembly process as well as impart solubility (*9*). The original proposed bio-inspired design is displayed in figure 1.
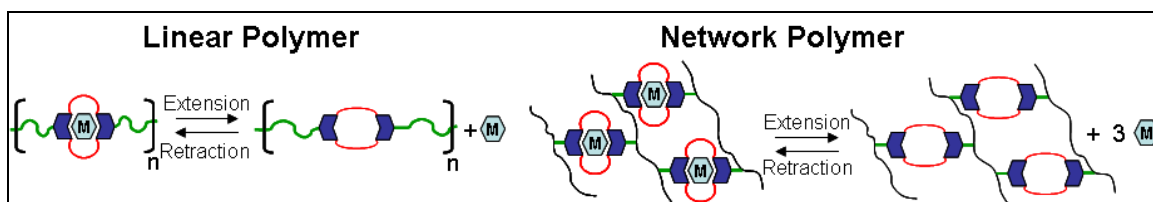
Figure 1. General scheme for modular metallo-supramolecular domains in linear and network polymers.

The proposed module consists of two 2,6-bis(1'-methylbenzimidazolyl)-4-oxypyridine (O-Mebip) units coordinated to a single metal ion. O-Mebip ligands are known to bind to a variety of metal ions and are synthetically accessible on large scales (*10*). The ligands are tethered by two alkyl linkers to provide a domain-like structure. However, upon further evaluation of the approach after submission of the proposal, the strategy for incorporating the metal-ligand modules was modified to streamline the synthetic process. The modified approach was based on a strategy where intra-molecular loops are formed within a single polymer chain to create a domain-like structure. A similar approach was successfully applied by Guan and coworkers using quadruple hydrogen-bonding units to form intra-molecular loops within a polyurethane polymer backbone (*11*). The intra-molecular loops imparted strength and toughness without sacrificing the ductility of the material. We propose a similar strategy using metal-ligand bonds rather than hydrogen bonds. Our revised strategy is outlined in figure 2.
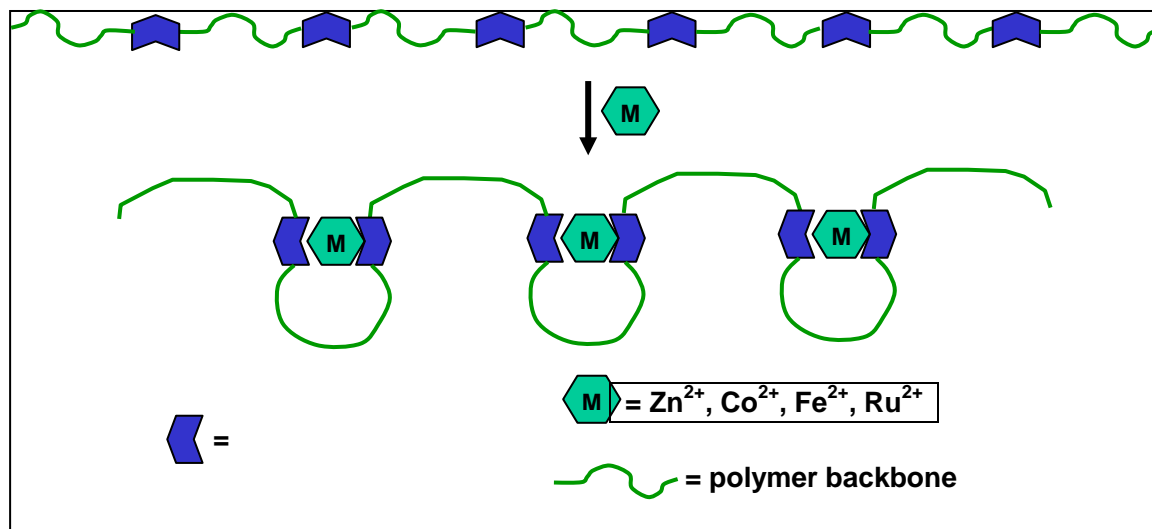

Figure 2. Revised general scheme for incorporating metal-ligand into polymer backbone to form intra-molecular loops for energy dissipation.

The current approach involves incorporating the ligand into the polymer main chain through an A + B step-growth polymerization. The ligand consists of 2,6-bisbenzimidazolylpyridine (BIP), which is known to bind to a variety of transition metals and is easily prepared with varied peripheral functionality (*12*). The ligand can be incorporated into a polymer backbone through reaction of the OH groups in an A+ B step-growth fashion. Under the appropriate conditions, the

metal can be added to form intra-molecular ditopic metal-ligand bonds. The revised scheme reduces the number of steps needed to prepare a domain-like structure and should provide an appropriate platform to study the "proof of concept" without investing significant time and effort in synthesis.

This report summarizes the synthesis and characterization of bio-inspired metallo-supramolecular polymers. Ultraviolet (UV) data are presented demonstrating the binding of various metals to the ligands imbedded in the polymer structure.

3. Results and Discussion

3.1 Ligand and Polymer Synthesis

The BIP ligand was prepared following a three-step protocol developed by Rowan and coworkers (figure 3) (*12*). The first step involved adding ethylamine to 2-chloro-4-nitroaniline via nucleophilic aromatic substitution of chlorine to provide amine 2 in 91% yield. Diacid chloride 4 was formed by a reaction of dicarboxylic acid 3 with thionyl chloride ($SOCl_2$) in the presence of a catalytic amount of dimethylformamide (DMF). Excess $SOCl_2$ was removed by distillation followed by the addition of amine 2 and DMF to the reaction vessel. After stirring overnight, sodium dithionite ($Na_2S_2O_4$), additional DMF, ethanol, and water were added to the reaction mixture and heated to reflux overnight to produce bisbenzimidazole 5 in 40% yield. A demethylation of compound 5 with boron tribromide (BBr_3) produced the BIP ligand in 90% yield. Overall, the BIP ligand was produced in 33% yield. We are currently optimizing this procedure to increase the overall yield, particularly in the preparation of compound 5.
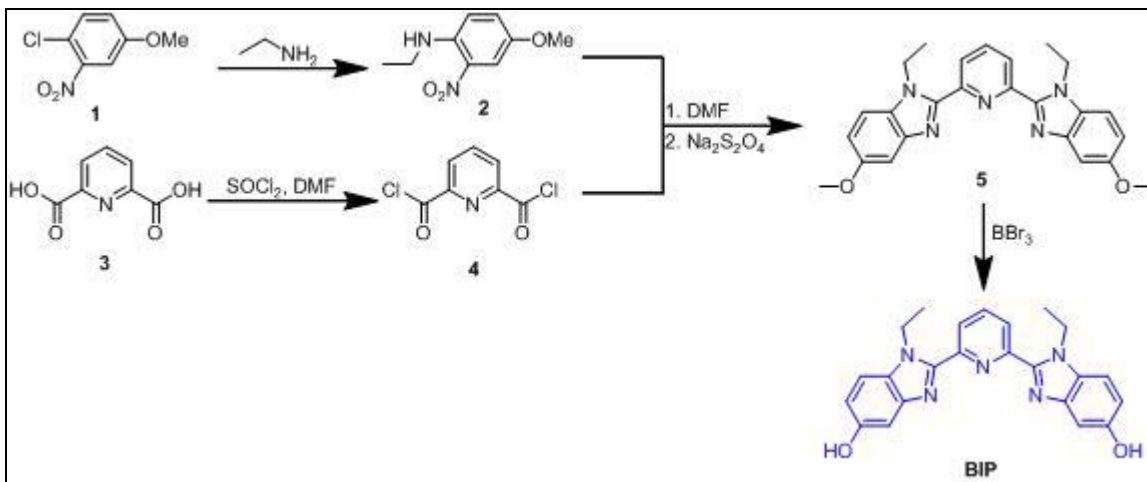

Figure 3. Three-step synthetic scheme for production of BIP ligand.

The peripheral OH groups provide a convenient functional handle to incorporate the ligand into a variety of polymer backbones such as polyurethanes, polycarbonates, or polyesters. However, we choose to explore using an obscure and relatively new polymerization method to integrate the BIP ligand into the main chain of a polymer backbone. The chemistry chosen is affectionately known as "thiol-ene click chemistry" and has been gaining significant momentum in recent literature (*13*). The reaction is highly versatile and quantitative, and can be conducted under a wide variety of conditions. The chemistry involves reaction between terminal thiols and terminal alkenes to form a thioether. Hoyle and coworkers (*14*) have recently demonstrated the feasibility of using thiol-ene click chemistry to produce polymers by a reaction of a difunctional alkene with a difunctional thiol in an A+B step-growth fashion. This type of polymer was chosen since the material could be prepared under mild reaction conditions and provides a backbone with a limited number of functional groups. Limiting the number of functional groups is important since it enables the effects associated with integrating metal-ligand bond into the polymer to be better correlated with the molecular structure. Using the appropriate reaction stoichiometry, a thiol terminated polymer can be produced, which can be further reacted, for example, to produce a polythiourethane (*14*). Synthesis of the ligand integrated polymer backbone via thiol-ene click chemistry is outlined in figure 4.
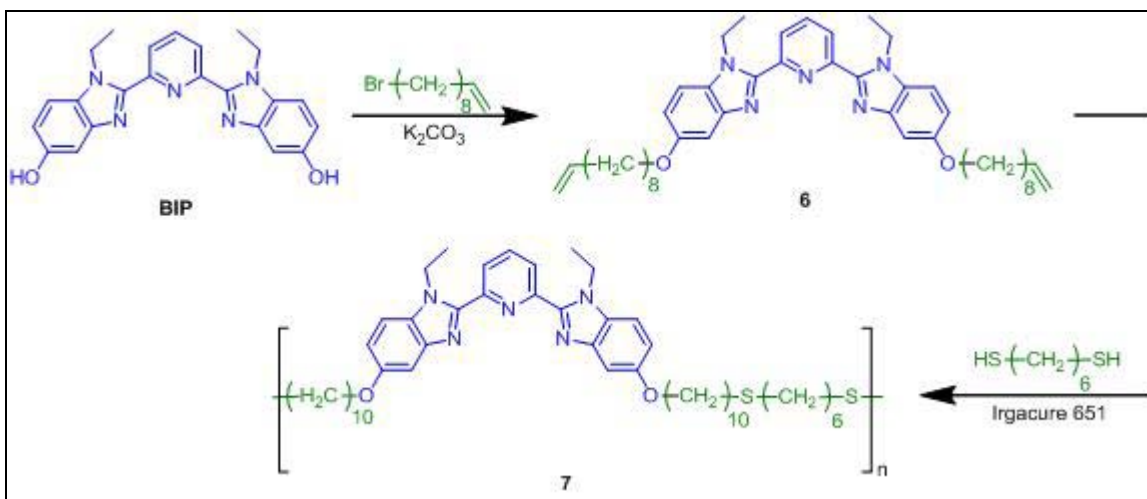

Figure 4.   Synthesis of a dialkene functional BIP ligand and A + B step-growth photopolymerization with hexanedithiol via thiol-ene click chemistry.

In order to incorporate the ligand via thiol-ene click chemistry, the BIP ligand needed to be further functionalized with terminal alkene groups. This was done be reacting BIP with an excess of 10-bromodec-1-ene in the presence of potassium carbonate (K_2CO_3) to produce dialkene 6 in 50% yield. This reaction produced a satisfactory amount of material to move forward but further optimization is required. Compound 6 was characterized by ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectrometry, which indicated it was pure (figure 5).
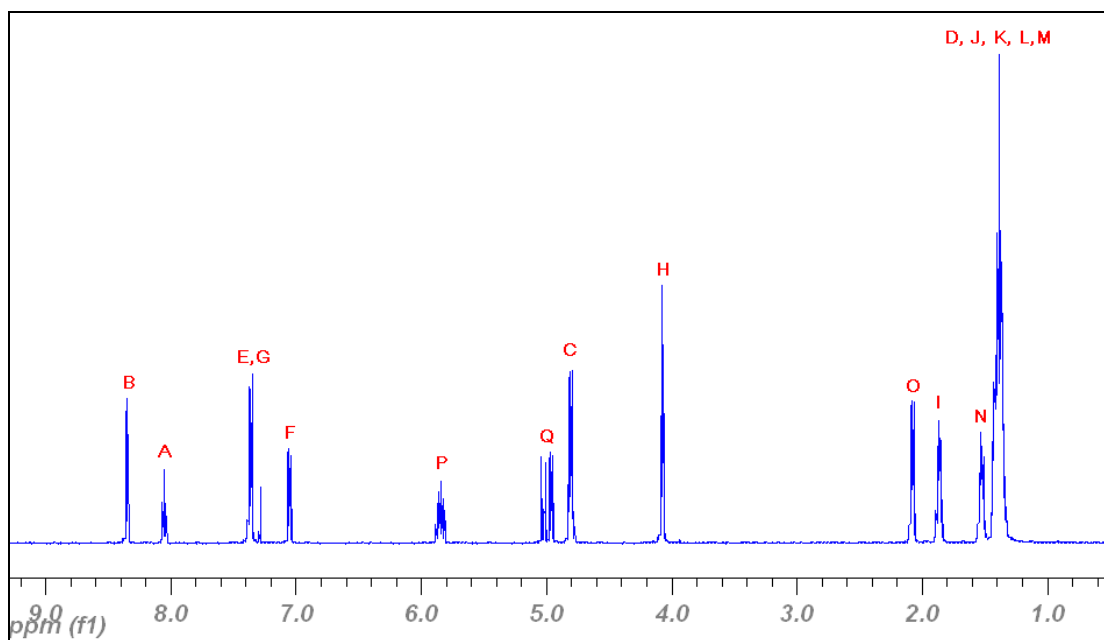
Figure 5. ^{1}H NMR of dialkene functionalized BIP ligand 6.

Thiol-ene click chemistry can be conducted under a variety of reaction conditions. Hawker and coworkers (*15*) recently surveyed a variety of conditions and determined a photochemical process to be the most robust, leading to the highest yields and shortest reaction times. Following their protocol, polymer 7 (in figure 4) was produced by reaction of dialkene 6 in a 1:1 molar ratio with hexanedithiol in the presence of photoinitiator Irgacure 651 under UV irradiation. Upon isolation, the polymer was characterized by ^{1}H NMR, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The results are presented in figures 6–8, respectively.
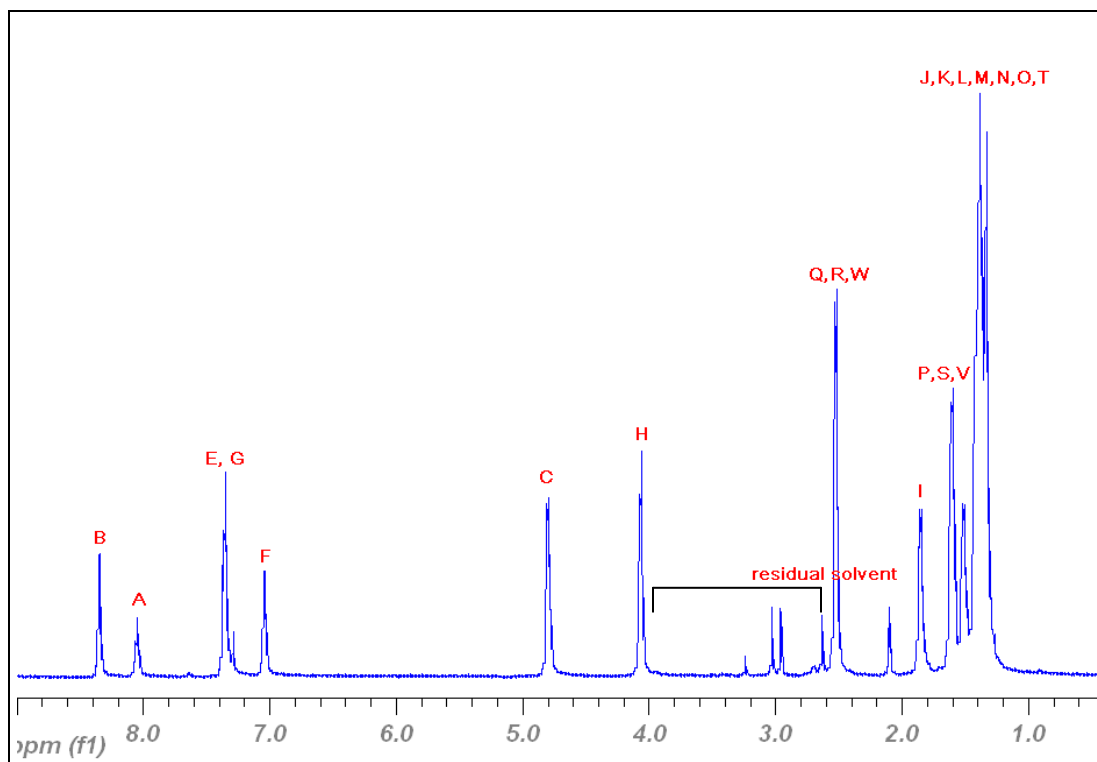
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Figure 6. ^{1}H NMR of polymer 7. The proton resonances associated with the terminal alkene functional groups in compound 6 are absent indicating complete reaction.
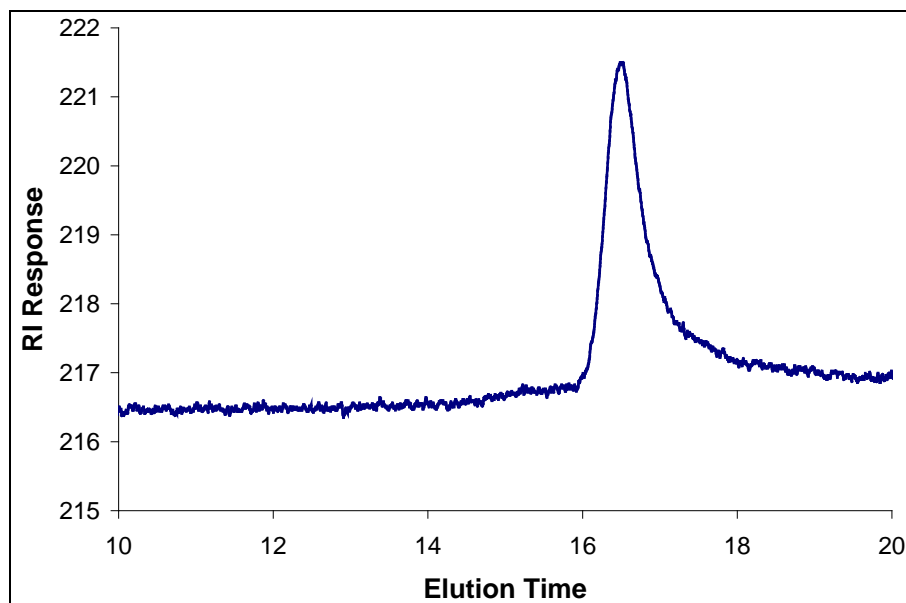

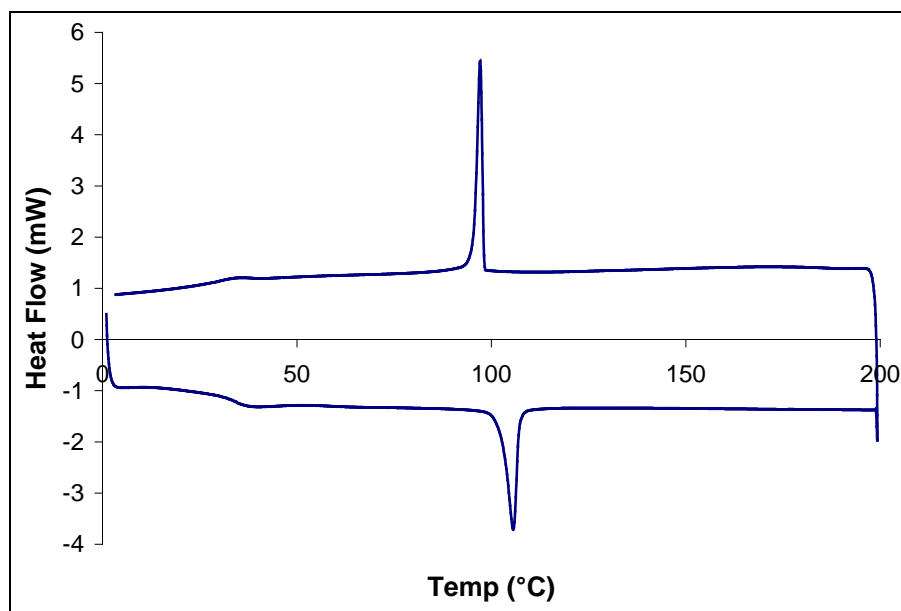Figure 7. GPC trace of polymer 7.

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Figure 8. DSC trace of polymer 7.

^{1}H NMR analysis indicated complete reaction of the terminal alkene functional groups as evidenced by the disappearance of resonances at 5.8 and 5.0 ppm associated with the vinylic protons (P and Q from figure 5). GPC analysis indicated high molecular weight polymer was formed with M_n = 92 kDa. DSC was performed to characterize the thermal properties of polymer 7. The material displayed a T_g of 34 °C and a melting transition at 104 °C. These results suggest the polymerization went to near quantitative conversion as the reactive functional groups on BIP derivative 6 were completely consumed, the polymer was of high molecular weight as evidenced by GPC, and the material displayed several thermal transitions by DSC.

3.2   Binding Properties of the Metallo-supramolecular Polymers

Formation of the metallo-supramolecular bond occurs through the simple addition of an appropriate metal salt to a dilute solution of ligand integrated polymers. Complexation of the metal ion to the ligands can be readily tracked by UV spectroscopy. Titration of the ligand-polymer solution allows one to track the UV absorbance associated with various species in solution (0:1, 1:1, 2:1 ligand-metal complex). Polymer 7 was titrated with $Co(ClO_4)_2$ and $Zn(ClO_4)_2$, and UV spectra were recorded with each increment (figures 9 and 10). Polymer 7 possessing the BIP ligand in the polymer backbone displayed an absorption maxima at 338 nm. Upon adding metal salt, the intensity of the absorption maxima began to decrease. Concurrently, a new peak began to emerge at roughly 390 nm, depending on the metal added. In both cases, the absorption intensity of the new peaks leveled off after the addition of 0.5 eq of metal ion, indicating the formation of a 2:1 metal-ligand binding complex.

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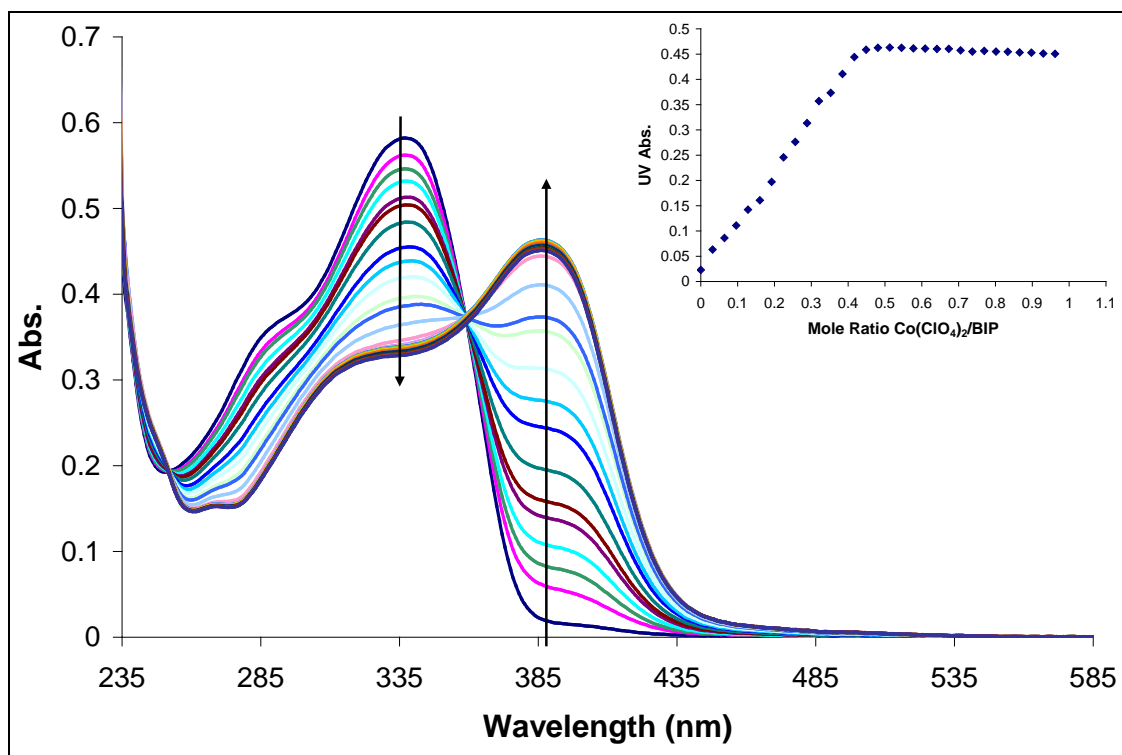Figure 9. UV titration experiment of polymer 7 with $Co(ClO_4)_2$. The inset shows the effect of absorbance at 385 nm with varying number of equivalents of metal ion.
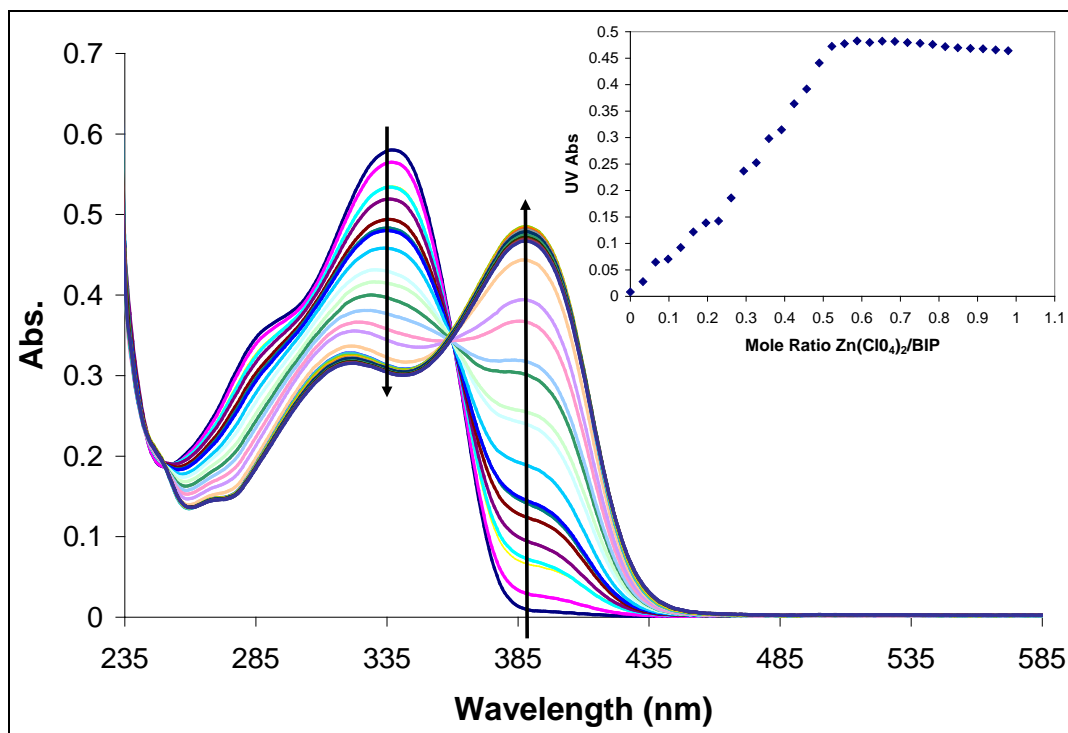

Figure 10. UV titration experiment of polymer 7 with $Zn(ClO_4)_2$. The inset shows the effect of absorbance at 390 nm with varying number of equivalents of metal ion.

4. Conclusions

The synthesis and characterization of a main-chain metallo-supramolecular polymer was reported. The BIP ligand was synthesized in 32% overall yield and was imbedded in the polymer backbone via photoinitiated thiol-ene click chemistry. Titration of the polymer with various hexa-coordinate transition metals with UV analysis demonstrated the binding of the metal with the ligand integrated polymers in a 2:1 ligand-to-metal ratio. This material is expected to demonstrate exceptional mechanical properties given the bio-mimetic modular structure as depicted in figure 2. The synthesis of ligand containing polymers is currently being optimized for scale up to provide a sufficient amount of material for mechanical characterization, including quasi-static and dynamic mechanical analysis methods.

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6. Transitions

The work presented in this DRI report is being transitioned to the Materials & Manufacturing Science (M&MS) PY01-10 Inverse Molecular Design Mission Program.

List of Symbols, Abbreviations, and Acronyms

AFM	atomic force microscopy
BBr_3	boron tribromide
BIP	2,6-bisbenzimidazolylpyridine
DMF	dimethylformamide
DRI	Director's Research Initiative
DSC	differential scanning calorimetry
GPC	gel permeation chromatography
K_2CO_3	potassium carbonate
M&MS	Materials & Manufacturing Science
$Na_2S_2O_4$	sodium dithionite
NMR	Nuclear Magnetic Resonance
O-Mebip	2,6-bis(1'-methylbenzimidazolyl)-4-oxypyridine
$SOCl_2$	thionyl chloride
UV	ultraviolet

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